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Communication: Vacuum ultraviolet photoabsorption of interstellar icy thiols

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Following the recent identification of ethanethiol in the interstellar medium (ISM) we have carried out Vacuum UltraViolet (VUV) spectroscopy studies of ethanethiol ($\text{CH}_3\text{CH}_2\text{SH}$) from 10 K until sublimation in an ultrahigh vacuum chamber simulating astrochemical conditions. These results are compared with those of methanethiol (CH_3SH), the lower order thiol also reported to be present in the ISM. VUV spectra recorded at higher temperature reveal conformational changes in the ice and phase transitions whilst evidence for dimer production is also presented. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4903840>]

I. INTRODUCTION

The identification of molecular species within any environment is often through spectroscopy, molecules having a distinctive “spectral fingerprint.” Spectroscopy is therefore used to identify molecules in planetary atmospheres and in the ISM.¹ The impending high resolution studies possible with next generation of telescopes (ALMA, JWST) have highlighted the need to expand the “spectroscopic database” both for larger molecular targets and into new regions of the electromagnetic spectrum (e.g., THz). However, an even greater challenge is to study the spectroscopy of molecules when they are in the condensed phase.¹ In the ISM, it is now recognised that many molecular species are synthesised on the surface of dust grains and remain within the icy mantles on these grains until desorbed or sputtered (e.g., during star or planetary formation processes).^{2–6} Spitzer has revealed the presence of molecular ices in the dense clouds of the ISM^{7–9} but it is the advent of ALMA and then JWST that is expected to reveal the chemical complexity of such ices. It remains a great challenge to study the spectroscopy of molecules in the condensed phase and to date most studies are constrained to the IR region through FTIR and Raman spectroscopy. There are fewer studies of VUV spectra of molecules in the condensed phase and until recently almost no THz studies. VUV spectra are important since they reveal the electronic state spectroscopy of molecules in the condensed phase, excitation of which can subsequently lead to local chemistry with the (photo)dissociation products synthesizing other chemical species. In the condensed phase many electronic states are “quenched” (e.g., Rydberg states) whilst the adiabatic energies of the valence states are shifted in energy (in the case of water by upwards of 1 eV) thus the chemistry and physics of condensed phase molecular solids are therefore, distinctly dif-

ferent from their corresponding gas phase.^{10–13} Accordingly, we have commenced an authoritative study of the VUV spectroscopy of molecular solids with particular focus on those species found in the ISM and on planetary surfaces.

Since the detection of methanol (CH_3OH) in Sgr A and Sgr B2¹⁴ and hydrogen sulphide (H_2S) in Sgr B2, and other sources,¹⁵ it was long expected that a molecule containing thiol group could be synthesized in the complex chemical regions of the ISM. In 1979, Linke *et al.*¹⁶ reported the first detection of methanethiol in Sgr B2. However, the first report on the detection of the higher order thiol, ethanethiol, has only been made recently¹⁷ in Orion KL, 30 years after the first observations of methanethiol, although the necessary precursors were detected earlier, ethylene in IRC +10216,¹⁸ ethanol in Sgr B2¹⁹ and hydrogen sulfide.

In this paper, we report the first condensed phase VUV spectra of two of the simplest thiols now identified in the ISM, ethanethiol, and methanethiol. By studying such spectra as a function of temperature we can provide some insight into the structure of these molecular solids and hence their likely reactivity within the ISM.

II. EXPERIMENTAL METHODOLOGY

The present experiments were carried out at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The VUV light source was the synchrotron radiation dispersed with a 6-m cylindrical grating monochromator. Four gratings were equipped in the monochromator among which the grating 450 grooves/mm was used for our measurements to cover the spectral range (107–240 nm; 11.6–5.2 eV). The minimum wavelength cutoff (107 nm) in these spectra was determined by the window material (Lithium fluoride; LiF) used as both the entrance and substrate window. The apparatus resolution was determined by the slit width (0.25×0.25 mm) of the monochromator. Spectra were

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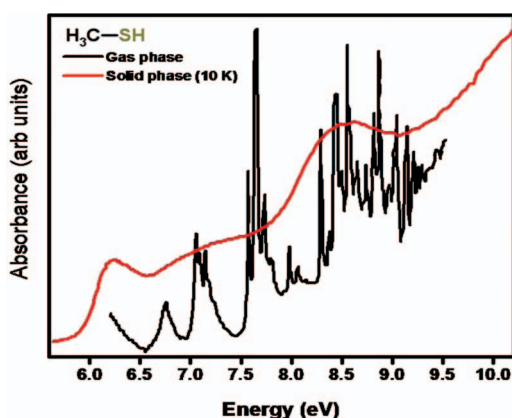


FIG. 1. VUV spectrum of methanethiol ice, formed at 10 K, compared with the gas phase spectrum.

recorded over the whole wavelength range in 0.5 nm steps. Samples were deposited on a precooled LiF window, kept at 10 K, that was enclosed in a vacuum chamber at pressures of the order of 10^{-9} mbar. After passing through the sample the VUV light irradiated a glass window coated with sodium salicylate which converts transmitted VUV light into visible light which as detected by a photomultiplier tube operating in photon counting mode (placed outside the chamber). Further details on the experimental setup can be found in our earlier publication.²⁰

Methanethiol and ethanethiol were purchased from Sigma Aldrich and Alfa Aesar with purity >99.5% and 97%, respectively. The vapour from samples of methanethiol and ethanethiol were allowed to form a uniform pure icy film of methanethiol and ethanethiol on the LiF substrate. Spectra were accumulated before and after deposition to obtain the incident (I_0) and transmitted (I_t) intensities from which absorbance spectra of the ice films were derived using the Beer-Lambert law. The temperature dependence of the VUV photoabsorption spectra were recorded by annealing the sample

to higher temperatures, which included, but were not limited to, 30 K, 50 K, 70 K, 90 K, 100 K, 120 K, 130 K and until sublimation.

III. RESULTS AND DISCUSSION

A. Methanethiol

The VUV spectrum of methanethiol recorded at 10 K was found to have strong absorption from 107 nm to 210 nm (11.6–5.9 eV) with two prominent, broad peaks at 8.6 eV and 6.2 eV and a third weak, broad peak at 7.2 eV (Figure 1). The gas phase photoabsorption spectrum of methanethiol in the VUV region contains three Rydberg series (4s, 4p, 4d, and 5p) 9.5–6.25 eV region. The vibrational structures of lower-energy Rydberg members are mainly assigned in terms of ν_5 , ν_6 , ν_7 , and ν_8 of the excited state²¹ which disappeared as expected in the ice phase.^{10,13} The broad peaks observed in the ice phase could be attributed as due to the absorption from first two triplet excited states of the molecule energetically shifted, which are not allowed otherwise in gas phase.

A spectrum recorded at 30 K (Figure 2(a)) was found to be similar to the spectrum recorded at 10 K except for a small change was observed in the absorption region between 6.2 and 6.6 eV (Figure 2(b)). Spectra recorded by annealing the sample to 50 K were found to be similar to that observed at 30 K. Further annealing to 70 K revealed a slight decrease in the 6.2 eV peak was observed and this intensity drop was found to be even more significant in spectrum recorded at 90 K. At this temperature the absorption intensity increased beyond 8 eV. The spectrum recorded at 100 K was found to be similar to the 90 K spectra until 9 eV after which a small drop in intensity was observed (Figure 2(a)). The spectrum recorded at 120 K was found to be similar to those at lower temperatures but with significantly reduced absorption intensity. No absorption peaks in the spectrum recorded at 150 K.

It is widely known^{10,12} that dimers can be formed whilst depositing the molecules at low temperatures (10 K). In the

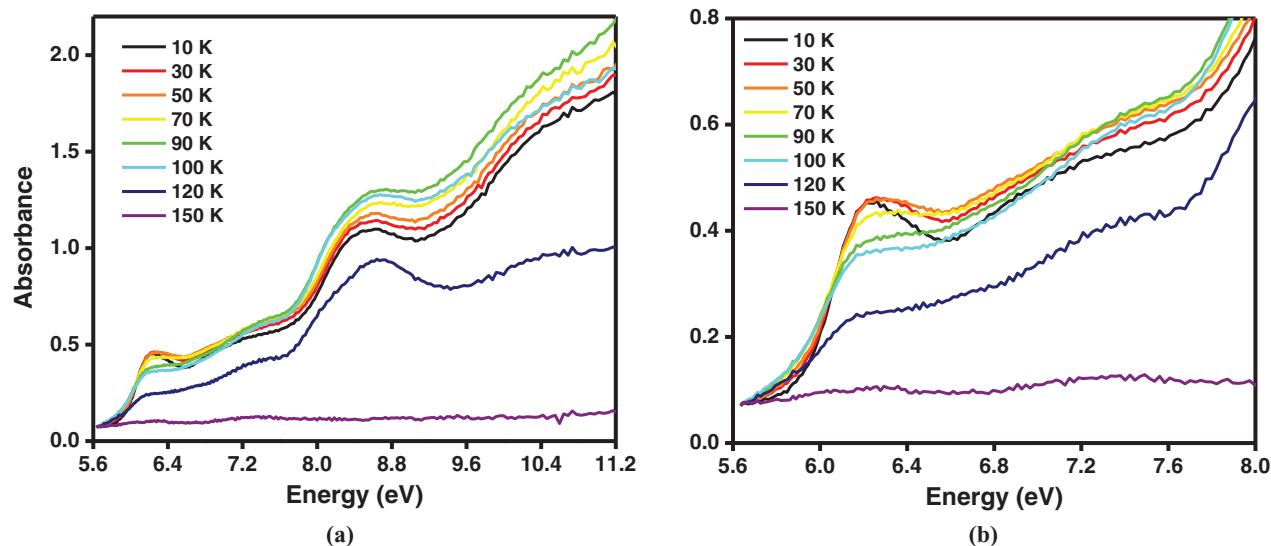


FIG. 2. Temperature dependent VUV spectra of methanethiol at different temperature (a) 5.6–11.2 eV and (b) 5.6–8.0 eV. Methanethiol was deposited on LiF substrate at 10 K and then annealed to higher temperatures.

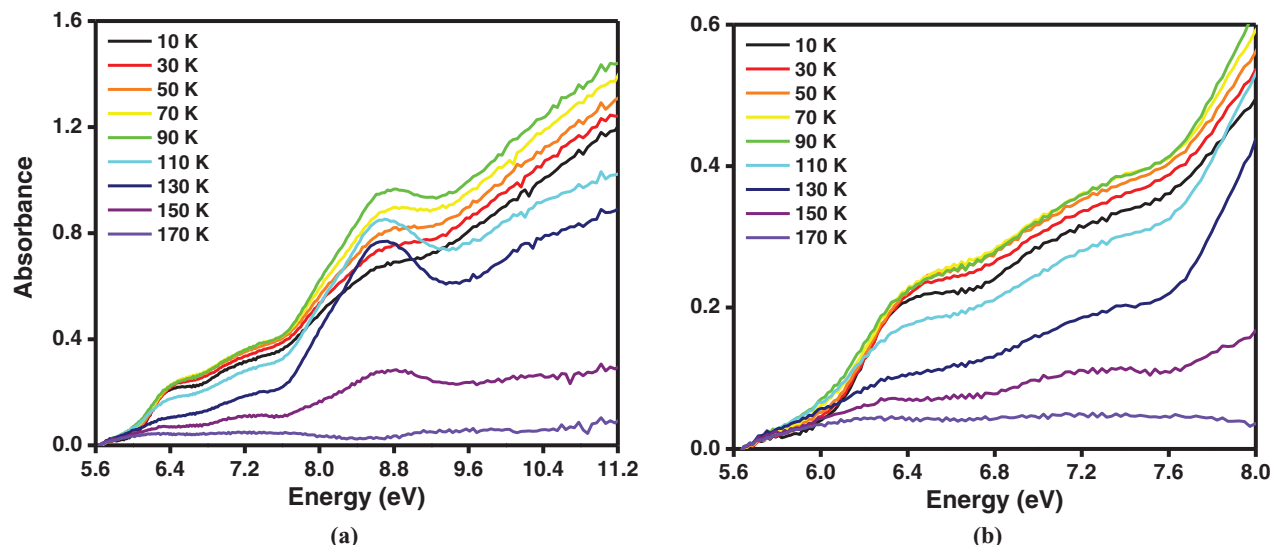


FIG. 3. Temperature dependent VUV spectra of ethanethiol at different temperature (a) 5.6–11.2 eV and (b) 5.6–8.0 eV. Ethanethiol was deposited on LiF substrate at 10 K and then annealed to higher temperatures.

methanethiol spectrum, the absorption band at 6.2 eV could be due to the formation of methanethiol dimers.²² Matrix isolation studies suggest that open chain dimers can be formed and there is a possibility of forming cyclic tetramers of methanethiol.²³ Upon annealing to higher temperatures, the changes observed in spectral shape, at lower energies, can be due to the conformational changes observed in the dimers of methanethiol due to the bonds that are made in the ice phase between the S-H...S atoms of methanethiol molecules, similar to the H-O...H interaction observed in formamide ices.^{13,24} The spectra at 90 K and at 100 K suggest reorientation has occurred within the ice matrix of methanethiol and from this we could conclude that there is a phase change from amorphous to crystalline, ortho-rhombic structure.²⁵ Methanethiol molecules started subliming off from the substrate above 120 K and all the ice has sublimed by 150 K.

B. Ethanethiol

The VUV spectrum of ethanethiol recorded at 10 K was found to have a strong absorption cross section between 107 nm and 210 nm (11.6–5.9 eV) with two prominent, broad peaks at 8.6 eV and 6.4 eV and a third weak, broad peak around 7.2 eV (Figure 3(a)). To the best of our knowledge, we could not find gas phase photoabsorption spectrum of ethanethiol in the VUV region, so a comparison with the gas phase spectrum could not be presented here.

The 10 K spectrum is very similar to that of the methanethiol. Spectra recorded at 30 K and 50 K were found to be similar to the spectrum recorded at 10 K albeit with a significant increase in the absorption cross section at energies above 8 eV (Figure 3(b)). Spectra recorded by annealing the sample to 70 K were found to be similar to that observed at 50 K but at 90 K the peak at 8.6 eV intensified. At this temperature intensity increase beyond 8 eV to the higher energy side was also observed. The spectrum recorded at 110 K has similar peak positions but all decreased intensity in compar-

ison with the spectrum recorded at 90 K (Figure 3(a)). The spectrum recorded at 130 K showed further reductions in the absorption intensity but the peak at 8.6 eV became very prominent and peak at 6.4 eV was found to be very weak. Further strong reduction in the absorption intensities were noticed in those two spectra recorded at 150 K and then at 170 K, respectively.

From the VUV spectra obtained at different temperatures it is very hard to discuss whether the ethanethiol molecular ice formed from vapour deposition contains either *trans* or *gauche* conformers and/ or both forms, since the difference between *trans* and *gauche* forms is known to be only 0.3 kcal mol⁻¹^{26,27} although the *gauche* conformer is the stablest form.²⁸ However, based on the Gibbs free energy difference of 1.92 kJ mol⁻¹ between *trans* and *gauche* forms, the relative abundances of *trans* and *gauche* forms were estimated to be 19% and 81%, respectively.²⁹ However, conformer-specific ionization spectroscopy studies on ethanethiol revealed only *gauche* conformer of ethanethiol to be present in a molecular jet.³⁰ Infrared studies recorded under identical environmental conditions to those used in the present experiment are needed if we are to reveal the nature of ethanethiol molecules formed at 10 K.

Nevertheless, in our experiment the VUV spectra demonstrate the bonding between S-H...S atoms of ethanethiol molecules through the appearance of an absorption band at 6.4 eV, similar to that observed at 6.2 eV within methanethiol ices. At 6.4 eV significant changes were not observed in the peak by annealing to higher temperatures, this could be due to the cyclic tetramers of ethanethiol molecules that are reported being more stable in the ice matrix²³ than the open chain dimers in methanethiol. However, the intensity and spectral shape changes in the absorption at the higher energies suggest molecular reorientation to have taken place within the ethanethiol ices upon annealing from 10 K to 110 K. By comparing the 90 K and 110 K spectra it is evident that a phase change from amorphous to crystalline started within the ices

at 110 K and is completed by further annealing and therefore the spectra at 130 K is that of a crystalline spectra of ethanethiol ice. At 150 K molecular sublimation was significant and by 170 K all the ethanethiol ice is lost from the surface.

IV. CONCLUSION

VUV spectra of methanethiol and ethanethiol were recorded over a range of temperatures, from which we can conclude that, upon deposition at lower temperatures, methanethiol and ethanethiol both form an amorphous ice that by annealing is transformed into a crystalline form at temperatures above 120 K. Absorption at longer wavelengths (lower energy region) suggests the formation of dimers which undergo rearrangement within the ice well before crystallization. In the case of ethanethiol ice, the dimers seem more stable than those in methanethiol. In order to obtain absolute VUV photoabsorption cross sections of methanethiol and ethanethiol in the condensed phase, our future laboratory simulation experiments will focus on deducing the methanethiol and ethanethiol ice density at conditions relevant to the ISM.

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